



(11)

EP 4 368 381 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.05.2024 Bulletin 2024/20

(51) International Patent Classification (IPC):
B29D 11/00 (2006.01)

(21) Application number: **22315268.7**

(52) Cooperative Patent Classification (CPC):
B29D 11/00009; B29D 11/00326; B29D 11/00865

(22) Date of filing: **09.11.2022**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(72) Inventors:
• **BIVER, Claudine**
31320 Vigoulet Auzil (FR)
• **CANO, Jean-Paul**
31650 Lauzerville (FR)

(74) Representative: **Plasseraud IP**
66, rue de la Chaussée d'Antin
75440 Paris Cedex 09 (FR)

(71) Applicant: **Essilor International**
94220 Charenton-Le-Pont (FR)

(54) **METHOD FOR MANUFACTURING AN OPHTHALMIC ARTICLE HAVING AT LEAST ONE MICROSTRUCTURED SURFACE, AND OPHTHALMIC ARTICLE THUS OBTAINED**

(57) The invention relates to a method for manufacturing an ophthalmic article having at least one microstructured surface, and to an ophthalmic article obtained by this method.

The method is for manufacturing an ophthalmic article having front and rear main surfaces, at least one of which is a microstructured surface, and comprises:

- Providing an ophthalmic substrate (10) with a substrate surface which is either hydrophobic or hydrophilic;
- Patterning the substrate surface to create thereon a surface wettability pattern comprising a two-dimensional array of distant hydrophilic micro-areas and of at least one hydrophobic zone which separates the hydrophilic micro-areas from each other;
- Coating the two-dimensional array with a hydrophilic liquid able to form an abrasion-resistant coating in a dried and/or cured state, to form distant droplets (D) of the hydrophilic liquid which are anchored to the hydrophilic micro-areas by wettability thereof; and
- Drying and/or curing the droplets (D) of the hydrophilic liquid, to generate therefrom a three-dimensional array of micro-lenses forming the at least one microstructured surface.

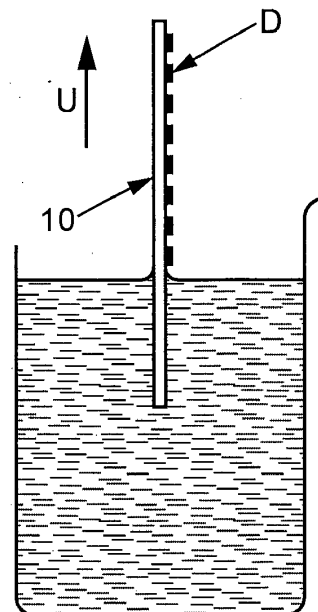


FIG. 10

EP 4 368 381 A1

Description**FIELD OF THE INVENTION**

[0001] The present invention relates to a method for manufacturing an ophthalmic article having at least one micro-structured surface, and to an ophthalmic article obtained by this method. The invention particularly applies to an ophthalmic lens comprising a three-dimensional array of micro-lenses configured to control evolution of myopia when the ophthalmic article is an ophthalmic curved prescription lens, even though the ophthalmic article may alternatively be incorporated into a smart eyewear device.

DESCRIPTION OF RELATED ART

[0002] Ophthalmic articles such as lenses generally comprise a base-lens substrate which is shaped in order to provide a desired optical power, and an abrasion-resistant coating (also known as anti-abrasion or hard coating) covering at least one surface of the base-lens substrate to prevent the latter from being damaged by scratches.

[0003] For a number of applications, it has been found desirable to provide on the base-lens substrate a plurality of micro-lenses, providing a local change of the power of the optical article. For instance, it is known from US 2017/0131567 A1 a lens comprising a plurality of micro-lenses formed on a surface of the lens, the local change of power provided by the micro-lenses enabling to slow down the progress of myopia.

[0004] Micro-lenses arrays are thus used for adding defocusing effect on a periphery of an ophthalmic corrective lens to control the evolution of myopia on kids. Indeed, some ophthalmic lenses are today specially designed and manufactured for that purpose. Nonetheless, this approach limits the extension of this technology to some materials, and the specific manufacturing process - which typically involves molds - induces extra costs and investments.

[0005] Existing molding processes of micro-lenses indeed require to protect the delicate micro-lenses surface with another covering material, and involve the conception and manufacturing of expensive and delicate molds. Specifically, such known processes typically inject a thermoplastic or thermosetting resin into a master mold containing a surface replication of the micro-lens array in an inverted profile. To protect the micro-lens array and guaranty a prolonged ophthalmic effect for the ophthalmic article, the molded micro-lenses are covered in a subsequent manufacturing step with the above-mentioned covering material, which results in that the focal lens defined by the micro-lens array is corrected due to the refractive index of the specific covering material. Further, this subsequent step is particularly delicate to control.

[0006] Apart from the fact that known molding manufacturing processes of prescription ophthalmic lenses are complex and costly, another drawback of these processes is that they are not versatile and limit the range of the molded ophthalmic articles that may be obtained, inasmuch as such processes cannot be easily implemented for all ophthalmic lens materials.

[0007] WO 2020/078964 A1 relates to an optical article comprising

- a base lens substrate, having a front surface and a back surface,
- an abrasion resistant coating covering at least one of said front surface and said back surface, the abrasion resistant coating having a first surface at the interface with the base lens substrate and a second surface opposite the first, and
- at least one optical element protruding from one of the first and second surfaces of said abrasion resistant coating, said optical element being composed of a material adapted to form an abrasion resistant coating and which may be formed of the same abrasion resistant coating by additive manufacturing, photolithography, thermal embossing or injection molding.

[0008] The article of Daniel M. Hartmann, Osman Kibar, and Sadik C. Esener, Characterization of a polymer microlens fabricated by use of the hydrophobic effect, July 1, 2000 / Vol. 25, No. 13 / OPTICS LETTERS 975, relates to means of fabricating hydrophilic domains in a hydrophobic background by lithographically patterning an adhesive hydrophobic layer. Polymer micro-lenses were fabricated by use of a dip-coating technique on a variety of mineral substrates (SiO₂, SiN, Ga As, InP, etc.), ranging in size from 2 μm to 500 μm in diameter.

[0009] It is to be noted that this article concerns optical systems in optics-based applications, but does not disclose an ophthalmic article, such as an ophthalmic lens or an eyewear article.

SUMMARY OF THE INVENTION

[0010] An object of the invention is to overcome at least the above-mentioned drawbacks, by providing a method for manufacturing an ophthalmic article having a front main surface and a rear main surface, at least one of which is a microstructured surface, by a simple additive process allowing to provide existing ophthalmic article of any material and geometry, such as curved prescription lenses, with an array of micro-lenses having a high mechanical resistance, so

as in particular to simplify the delivery of a full range of myopia controlling lenses without changing the underlying lens blank, nor the supply chain of finished lenses.

[0011] According to the invention, this manufacturing method comprises the following steps:

- a) Providing an ophthalmic substrate with a substrate surface which is either hydrophobic or hydrophilic;
- b) Patterning the substrate surface to create thereon a surface wettability pattern comprising a two-dimensional array of mutually distant hydrophilic micro-areas and of at least one hydrophobic zone which separates the hydrophilic micro-areas from each other;
- c) Coating the two-dimensional array with a hydrophilic liquid which is able to form an abrasion-resistant coating in a dried and/or cured state, to form mutually distant droplets of the hydrophilic liquid which are anchored to the hydrophilic micro-areas by wettability thereof; and
- d) Drying and/or curing (e.g. by UV or thermal curing) the mutually distant droplets of the hydrophilic liquid, to generate therefrom a three-dimensional array of micro-lenses forming the at least one microstructured surface.

[0012] It is to be noted that this "post manufacture" according to the invention of the array of micro-lenses onto the front main surface and/or the rear main surface of the ophthalmic article, by means of the addition of the abrasion-resistant coating in steps c) and d), is fully compatible with the prescription organization and technology standards.

[0013] It is also to be noted that the manufacturing method of the invention allows to create a pattern of micro-lenses array on an existing ophthalmic article, such as a prescription lens, without changing the manufacturing process of the lens, which may be made of any lens material and may have any geometry, as explained above. As a consequence, the whole process may advantageously be implemented at a lower cost and allows late personalization of the micro-lenses, compared to existing processes.

[0014] It will also be noted that a major advantage of the manufacturing method of the invention is that the array of micro-lenses may be made of any existing abrasion-resistant (i.e. hardcoat) material with a high mechanical resistance, so that these micro-lenses do not require any other protection layer thereon (even though an additional layer, such as an antireflection coating *inter alia*, may optionally be applied onto the outer surface of the micro-lenses).

[0015] It will further be noted that in the case of a mineral ophthalmic substrate, the surface of the mineral ophthalmic substrate may be rendered either hydrophobic or hydrophilic by an appropriate treatment, and that steps b), c) and d) above may be applied to any mineral or organic ophthalmic substrate in the uncoated state (to either a "neat substrate" or a modified substrate surface), provided that the ophthalmic substrate has an abrasion resistance which is high enough.

[0016] According to a first embodiment of the invention, step a) comprises rendering the ophthalmic substrate, which consists of a mineral material, either hydrophobic or hydrophilic on said substrate surface (i.e: without necessarily providing in step a) the ophthalmic substrate with a separate hydrophobic or hydrophilic coating).

[0017] According to a second embodiment of the invention, step a) comprises providing the ophthalmic substrate, which consists of an organic material, with a first abrasion-resistant coating which is either hydrophobic or hydrophilic and defines said substrate surface, and the abrasion-resistant coating which forms the micro-lenses after steps c) and d) thus represents a second abrasion-resistant coating.

[0018] Thickness of said first abrasion resistant coating ranges generally from 1 micrometer to 10 micrometers, preferably from 2 to 6 micrometers.

[0019] It may be noted that such a first abrasion-resistant coating may also be applied to a mineral ophthalmic substrate, although not being necessary.

[0020] As detailed below, it will further be noted that the three-dimensional array of micro-lenses obtained in step d) according to the above first and second embodiments may be removable, for instance by dipping in an appropriate removing bath while protecting the first abrasion-resistant coating, so as to selectively recover the ophthalmic substrate coated with the first abrasion-resistant coating. This may advantageously allow to recoat the ophthalmic substrate provided with the first abrasion-resistant coating with another three-dimensional array of micro-lenses, in order to change the optical properties of the ophthalmic article according to the evolution of the wearer's myopia. This may also be useful in case of a low yield obtained during the creation of the first three-dimensional array of microlenses, because its removal will allow a second pass which is hardly feasible for polymeric microlenses made by an injection process.

[0021] According to another feature of the above second embodiment of the invention, in step c) the hydrophilic liquid may be selected so that the second abrasion-resistant coating forming the micro-lenses has a Bayer value preferably greater than or equal to the Bayer value of the first abrasion-resistant coating, both Bayer values being measured in accordance with the ASTM F735-81 standard and being preferably greater than or equal to 2, more preferably of between 3 and 25 and even more preferably of between 4 and 15, depending of the materials used for the second abrasion-resistant coating.

[0022] This gradient in Bayer values between the first and second abrasion-resistant coatings particularly allows to impart a satisfactory mechanical resistance to the micro-lenses.

[0023] Advantageously according to any of the preceding features according to the above first and second embodi-

ments, in step c) the hydrophilic liquid may be a polar liquid selected from solutions in a polar solvent and emulsions comprising a polar phase.

[0024] It will be noted that these solutions or emulsions in polar solvents, which may be highly polar, include a mixture of highly polar liquids, and that such an exemplary hydrophilic liquid may contain a low quantity of water.

[0025] It will also be noted that the hydrophilic liquid may be further selected to exhibit a low enough viscosity and a high enough surface tension, which are configured to minimize viscous drag forces and maximize capillary forces in order to oppose wetting of the at least one hydrophobic zone by the hydrophilic liquid.

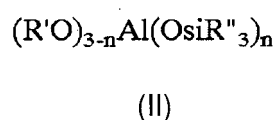
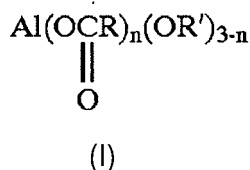
[0026] It will further be noted that the hydrophilic liquid composition may be further selected based upon the desired refractive index for the array of micro-lenses.

[0027] Preferably, according to the above first and second embodiments the hydrophilic liquid used in step c) comprises at least one inorganic oxide of a metal or non-metal selected from colloidal silica, titania, zirconia, antimony oxide and mixtures or composite oxide(s) thereof, and the hydrophilic liquid is selected from polar solutions comprising alcoholic, ketones and/or ester solvents, the hydrophilic liquid comprising a silane or alkoxy silane hydrolysate/ condensate, the at least one inorganic oxide and a catalytic amount of a curing catalyst preferably selected from aluminum-based catalysts and organometallic complexes of zirconium, titanium, iron or nickel.

[0028] Alternatively, the hydrophilic liquid composition may be devoid of colloidal oxide particles. In this case, the hydrophilic liquid composition may essentially contain silane or alkoxy silane hydrolysates/ condensates in polar solvents.

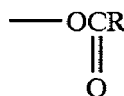
[0029] The hydrophilic liquid more preferably comprises an epoxytrialkoxysilane and dialkyldialkoxysilane hydrolysate/ condensate, a colloidal silica and a catalytic amount of the curing catalyst. Exemplary usable compositions are disclosed in document FR2702486 A1 or its equivalent US 2003/165698 A1, and also in WO 2020/078964 A1. The remainder of the hydrophilic liquid composition may be essentially composed of solvents conventionally used for the formulation of such hydrophilic liquids. Still more preferably, the hydrolysate/ condensate is a γ -glycidoxypolytrimethoxysilane (GLY-MO) and dimethyldiethoxysilane (DMDES) hydrolysate/ condensate, or else a GLYMO and triethyl orthosilicate (TEOS) hydrolysate/ condensate.

[0030] The exemplary aluminum-based curing catalyst may be selected from aluminum chelates or compounds with one of the two following formulae (I) or (II):



wherein:

- R and R' are linear or branched alkyl groups with 1 to 10 carbon atoms,
- R'' is a linear or branched alkyl group with 1 to 10 carbon atoms, a phenyl group, a



- group where R has the meaning given above,
- and n is a whole number from 1 to 3.

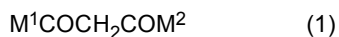
[0031] An aluminum chelate knowingly is a compound formed by reacting an aluminum alcoholate or acylate with nitrogen- and sulphur-free sequestering agents which contain oxygen as the coordinating atom.

[0032] The aluminum chelate is preferably selected from compounds having formula (III):



wherein:

- X is an OL group where L is an alkyl group with 1 to 10 carbon atoms,
- Y is at least one coordinating product obtained from a compound having formula (1) or (2) below:



wherein:

M^1 , M^2 , M^3 and M^4 are alkyl groups with 1 to 10 carbon atoms, and v takes the value 0, 1 or 2.

[0033] Examples of compounds having formula (III) are aluminum acetylacetonate, aluminum ethylacetoacetate bisacetylacetonate, aluminum bisethylacetoacetate acetylacetonate, aluminum di-n-butoxide monoethylacetoacetate and aluminum diisopropoxide monomethylacetoacetate.

[0034] Preferred compounds having formula (I) or (II) are those where R' is an isopropyl or ethyl group and R and R'' are methyl groups.

[0035] One or more compounds having formula (I), (II) or (III) can be used as the aluminum-based curing catalyst, which catalyst may be used in a proportion which will harden the hydrophilic liquid over a period of a few hours at temperatures in the order of 100°C, generally in a proportion of 0.1% to 5% by weight of the hydrophilic liquid composition.

[0036] According to a preferred embodiment of the invention common to the above first and second embodiments, step c) is implemented via dip coating, by dipping the ophthalmic substrate provided with the substrate surface once patterned (therefore provided with the first abrasion-resistant coating, according to the second embodiment) into a bath of the hydrophilic liquid and afterwards by a controlled withdrawal of the dipped ophthalmic substrate from the bath, the withdrawal being controlled so as to obtain a desired curvature radius and/or volume for each of the micro-lenses obtained in step d). Indeed, the curvature radius of each droplet is a consequence of the droplet volume, which is itself directly linked to the withdrawal speed, assuming that this speed is inferior to a critical speed. Besides, the droplet volume also depends upon the dimensions of each hydrophilic micro-area and of the at least one zone created in step b).

[0037] It is to be noted that this dip coating technique is preferred for coating the two-dimensional array with the hydrophilic liquid, even though other coating techniques such as spin coating, spray coating or roll coating may alternatively be used.

[0038] In the dip coating preferably implemented in step c), a maximum allowable withdrawal speed may be determined, by measuring a critical transition speed where no film of the hydrophilic liquid is dragged onto the at least one hydrophobic zone once dipped and withdrawn, and the controlled withdrawal of the dipped ophthalmic substrate from the bath is implemented at an adjusted withdrawal speed selected to be lower than or equal to said critical transition speed.

[0039] According to general features of the invention which may relate to any of the preceding ones, including the above first and second embodiments, and particularly when step c) is implemented by dip coating, steps b) and c) may be implemented so that the micro-lenses obtained in step d) have:

- at least one greater transverse direction, such as a diameter, which is greater than 500 μm and preferably of between 1 mm and 2 mm in case the micro-lenses are designed for controlling evolution of myopia when the ophthalmic article is an ophthalmic curved prescription lens; and/or
- at least one shape selected from spherical, cylindrical, ellipsoidal and combinations thereof, even though there is no limitation for the obtained shape(s) of the micro-lenses; and/or
- various refractive indexes and/or various colors, and may optionally be hazy.

[0040] It is to be noted that the shape and size of the droplets anchored in step c) of the method of the invention determine the radius and focal parameter of the array of micro-lenses, after subsequent drying and/or curing in step d). Indeed, the final shape of the droplets is different from the droplets shape immediately after said withdrawal, due to evaporation of the solvent used in the abrasion-resistant coating for the droplets. Furthermore, the dry content of this coating liquid may also be a control parameter of the final geometry of the micro-lenses.

[0041] It is also to be noted that variations from the conventional spherical shape of the micro-lenses may be easily obtained by varying the geometry of the hydrophilic micro-areas in step b), including different sizes and/or shapes which may be easily combined for the micro-lenses obtained on a same surface in step d), leading for instance to astigmatic micro-lenses and/or to micro-lenses of different optical powers (e.g. two types of spherical micro-lenses in order to create two optical powers).

[0042] According to general features of the invention which may relate to any of the preceding ones, including the above first and second embodiments, and particularly when step c) is implemented by dip coating:

- the ophthalmic substrate may consist of a mineral material, or of an organic material which is thermosetting, photocurable or thermoplastic; and
- the method may further comprise at least one of steps A) and B) below:

A) coating the ophthalmic substrate before step a) with a primer coating which is itself coated with said substrate surface (i.e. coated with the first abrasion-resistant coating in the second embodiment), and
 B) laminating the ophthalmic substrate provided with the patterned substrate surface on an existing curved lens (for instance based on either a thermoplastic or thermosetting material and already including or not an abrasion-resistant coating), by a forming technique implemented by laminating

- between step b) and step c), the ophthalmic substrate provided with said substrate surface patterned according to the surface wettability pattern, or

- after step d), the ophthalmic substrate provided with the patterned substrate surface (i.e. with the patterned first abrasion-resistant coating in the second embodiment) and the three-dimensional array of micro-lenses.

[0043] In the second embodiment, could be alternatively implemented as a variant of step B), between step a) and b), the lamination of the ophthalmic substrate provided with the first abrasion resistant coating, not yet patterned.

[0044] Also in relation to the second embodiment, the first abrasion-resistant coating may be selected from solutions comprising at least one inorganic oxide selected from metal and non-metal oxides.

[0045] By way of thermoplastic material usable for the ophthalmic substrate, mention may be made e.g. of polyamides, polyimide, polysulfones, polycarbonates and copolymers thereof, polyethylene terephthalate and (meth)acrylic (co)polymers, particularly polymethylmethacrylate (PMMA). Mention may also be made of cyclic olefin copolymers (COC), cyclic olefin polymers (COP) and also cellulose acetate, such as tricellulose acetate (TAC).

[0046] By way of thermosetting materials usable for the ophthalmic substrate, mention may be made e.g. of:

- homopolymers and copolymers of allyl carbonates of linear or branched aliphatic or aromatic polyols, such as homopolymers of diethylene glycol bis(allyl carbonate) (CR 39®),
- homopolymers and copolymers of (meth)acrylic acid and esters thereof, which are optionally derived from bisphenol A,
- homopolymers and copolymers of thio(meth)acrylic acid and esters thereof,
- homopolymers and copolymers of allyl esters which are optionally derived from bisphenol A or phthalic acids, and allyl aromatics such as styrene,
- copolymers of urethane and thiourethane,
- homopolymers and copolymers of epoxy, and
- homopolymers and copolymers of sulfide, disulfide and episulfide;

[0047] Examples of substrates usable in the present invention include those obtained from MR6®, MR7®, MR8®, MR174® and MR10® resins (thermosetting polythiourethane resins), CR39® and Trivex®.

[0048] As for the first abrasion-resistant coating which is used in the above second embodiment of an organic ophthalmic substrate (this coating being optional in the above first embodiment of a mineral ophthalmic substrate), it may consist of a composition similar to that described above for the hydrophilic liquid designed to form the second abrasion-resistant coating, i.e. in which the metal or non-metal oxide is selected from colloidal silica, titania, zirconia, antimony oxide and mixtures thereof, the first abrasion-resistant coating deriving from a polar solution comprising alcoholic, ketones and/or ester solvent and comprising an epoxysilane hydrolyzate, the at least one inorganic oxide and a catalytic amount of a curing catalyst, preferably an aluminum-based curing catalyst which may be selected from one of the above formulae (I), (II) or (III). Nonetheless, the first abrasion-resistant coating is preferably selected so as to exhibit a Bayer value greater than or equal to 2 and preferably lower than or equal to the Bayer value of the second abrasion-resistant coating, both values being measured according to ASTM F735-81.

[0049] Regarding the optional supplemental steps A) and B) mentioned above, it may be noted that:

- step A) of coating the ophthalmic substrate before step a) with a primer coating with a high surface tension may allow to improve adhesion of the abrasion-resistant coating on some substrates and to confer also an impact resistance on the finished ophthalmic article; and that
- step B) may include the case where the micro-lenses are made of a film obtained by the sequence of steps a) to d), this film being afterwards laminated on an existing ophthalmic article which may optionally already be provided with an abrasion-resistant coating (e.g. laminated on a curved prescription lens bearing a hardcoat or not).

[0050] According to another general feature of the invention which may relate to any of the preceding ones, including the above first and second embodiments, and particularly when step c) is implemented by dip coating, the method may further comprise the following steps:

e) removing the three-dimensional array of micro-lenses obtained in step d) by dipping in a removing bath and optionally providing said substrate surface (i.e. the first abrasion-resistant coating in the second embodiment) with protective masking means, so as to selectively recover the ophthalmic substrate provided with the substrate surface, and

f) implementing at least once the sequence of steps c) and d) and optionally of step b) firstly, to obtain another three-dimensional array of micro-lenses forming the at least one microstructured surface (indeed, step b) may not be necessarily implemented again in step f), if the removal of the micro-lenses leads to a surface having hydrophilic properties).

[0051] It may be noted that depending upon the respective compositions of the first and second abrasion-resistant coatings, the dipping in said removing bath may undesirably remove both coatings as may particularly be the case in a caustic bath (which is usable inter alia for said removing bath), hence said protective masking means in order to protect the first abrasion-resistant coating during this dipping e.g. in a caustic bath, to remove only the second abrasion-resistant coating. Nonetheless, it may be desirable to remove both coatings, in case the first abrasion-resistant coating has been damaged. Then, it is possible to implement again the whole process.

[0052] It may also be noted that said protective masking means may be subsequently kept to apply another array of micro-lenses in step f).

[0053] According to another general feature of the invention which may relate to any of the preceding ones, including the above first and second embodiments, and particularly when step c) is implemented by dip coating, step a) may be implemented by using, by way of the ophthalmic substrate provided with said substrate surface (i.e. with the first abrasion-resistant coating in the second embodiment), an ophthalmic lens selected from a finished ophthalmic lens and an ophthalmic lens blank optionally edged, preferably an ophthalmic curved prescription lens.

[0054] According to another general feature of the invention which may relate to any of the preceding ones, including the above first and second embodiments, and particularly when step c) is implemented by dip coating, step b) may be implemented by a mask-assisted or maskless technique selected from chemical etching, laser ablation or etching (in maskless laser etching, the pattern is digitally created by laser scanning of the surface), low pressure or atmospheric plasma or corona etching, UV or ozone etching and Reactive Ion Etching (RIE), chemical grafting of molecules bearing hydrophilic or hydrophobic functions, to create the hydrophilic micro-areas and the at least one hydrophobic zone on the substrate surface (i.e. on the first abrasion-resistant coating in the second embodiment).

[0055] Step b) may be implemented by a mask-assisted technique by

(i) patterning said substrate surface (i.e. the first abrasion-resistant coating in the second embodiment) which is selected to be hydrophobic, preferably by a chemical etching technique assisted with a flexible mask applied under pressure onto the substrate surface or by

(ii) beforehand providing in step a) the substrate surface (i.e. the first abrasion-resistant coating in the second embodiment) with an outer surface which is either already hydrophilic or is rendered hydrophilic between steps a) and b), and creating in step b) the at least one hydrophobic zone via said mask-assisted technique by treating unmasked areas with said molecules bearing hydrophobic functions.

[0056] Alternatively, step b) may preferably be implemented by a maskless surface ablation technology which uses a power laser scanning (e.g. an Excimer laser, with picosecond or femto second technologies) or by a maskless technology (such as photolithography), instead of a technology using a contact or projected image mask.

[0057] More preferably, according to the second embodiment, step b) is implemented in case (i) by providing the flexible mask with an array of through micro-holes optionally having different shapes and/or dimensions, the through micro-holes preferably having a diameter of between 1 mm and 2 mm, and by immersing the first abrasion-resistant coating in a caustic bath of NaOH or KOH, and

in case (ii), the outer surface of the first abrasion-resistant coating may advantageously be rendered hydrophilic between steps a) and b) by:

- at least one of chemical etching, laser ablation or etching, low pressure or atmospheric plasma or corona etching, UV or ozone etching and Reactive Ion Etching (RIE), and chemical grafting of molecules bearing hydrophilic functions, or by
- depositing onto the first abrasion-resistant coating layer a hydrophilic layer comprising at least one inorganic oxide of a metal or non-metal selected from silica, titania, zirconia, antimony oxide and mixtures thereof.

[0058] It may be noted that in case (ii) above, the same pattern of hydrophilic micro-areas and hydrophobic zone may be created as starting from a hydrophobic first abrasion-resistant coating, by using or rendering the outer surface of the first abrasion-resistant coating totally hydrophilic for instance by:

- initially using a hydrophilic material for the first abrasion-resistant coating; or by
- a mask-assisted or maskless technique selected from chemical etching, laser ablation or etching, low pressure or atmospheric plasma or corona etching, UV or ozone etching, RIE and chemical grafting of molecules bearing hydrophilic functions, or by
- adding said hydrophilic layer for example of silica or titanium oxide.

[0059] So, case (ii) above could be useful for instance if the first abrasion-resistant coating was not hydrophobic enough to create, according to case (i) above, enough wettability contrast between the hydrophilic micro-areas and the at least one hydrophobic zone. Alternatively, case (i) may be implemented by firstly adding in step a) a specific highly hydrophobic coating to the slightly hydrophobic first abrasion-resistant coating, so as to increase the wettability contrast in step b).

[0060] An ophthalmic article according to the invention is obtained by a method as defined above, the ophthalmic article having a front main surface and a rear main surface, at least one of which being a microstructured surface, and the ophthalmic article comprises:

- an ophthalmic substrate provided with a patterned substrate surface (i.e. with the first abrasion-resistant coating in the second embodiment) which is patterned according to a surface wettability pattern comprising mutually distant hydrophilic micro-areas and of at least one hydrophobic zone which separates the hydrophilic micro-areas from each other, the ophthalmic substrate preferably being organic, and
- a three-dimensional array of micro-lenses which form the at least one microstructured surface and are respectively anchored to the sole hydrophilic micro-areas, the micro-lenses being based on an abrasion-resistant coating which coats the patterned substrate surface.

[0061] In case the ophthalmic substrate consists of an organic material according to the second embodiment, said substrate surface being defined by a first abrasion-resistant coating which is patterned according to said surface wettability pattern, said abrasion-resistant coating forms a second abrasion-resistant coating which coats the patterned first abrasion-resistant coating and which preferably has a Bayer value greater than or equal to the Bayer value of the first abrasion-resistant coating, both Bayer values being measured in accordance with the ASTM F735-81 standard.

[0062] Advantageously, the ophthalmic article may be selected from:

- ophthalmic lenses, including finished ophthalmic lenses and ophthalmic lens blanks optionally edged, preferably curved prescription lenses for controlling evolution of myopia, in which the micro-lenses have at least one shape selected from spherical, cylindrical, ellipsoidal and combinations thereof and at least one greater transverse direction, such as a diameter, which is greater than 500 μm and preferably of between 1 mm and 2 mm, and
- smart eyewear devices.

[0063] As explained above, an ophthalmic article according to the invention, such as an ophthalmic lens for spectacle glasses, may include micro-lenses which may have various refractive indexes and/or various colors, which may optionally be hazy and which may be coated with various coatings, such as at least one coating for example selected from antireflective coatings, antistatic coatings, conductive coatings, antifog coatings, anti-smudge coatings, photochromic coatings, electrochromic coatings, polarized coatings and combinations thereof.

[0064] It will be noted that the ophthalmic article may not only be a corrective lens usable to treat or control myopia, but also to treat or control hyperopia, astigmatism and/or presbyopia.

DESCRIPTION OF DRAWINGS

[0065]

Figure 1 is a schematic side view of a hydrophilic micro-area illustrating the theory of total wetting of the area by a hydrophilic liquid;

Figure 2 is a schematic side view of a partially hydrophobic zone illustrating the theory of partial wetting of the zone by a hydrophilic liquid, by showing the contact angle θ_c as a function of the solid-vapor, solid-liquid and liquid-vapor interfacial energies γ_{SG} , γ_{LS} and γ_{LG} , respectively;

Figure 3 is a schematic side view of a highly hydrophobic zone illustrating a poor wetting of the zone by a hydrophilic liquid shown by a contact angle greater than 90° ;

Figure 4 is a schematic side view of a surface wettability pattern according to the invention comprising a two-dimensional array of a hydrophobic zone and hydrophilic micro-areas, which are coated with a hydrophilic liquid forming mutually distant droplets anchored to the hydrophilic micro-areas by total wettability thereof;

Figure 5 is a schematic top view of a droplet of hydrophilic liquid surrounded by the hydrophobic zone, the droplet being configured to form a non-axisymmetric micro-lens;

Figure 6 is a diagrammatic representation for sag calculation of hemispherical micro-lenses for controlling myopia that may be formed according to the invention, based on the radius of curvature R and the diameter d of a micro-lens;

Figure 7 is a diagrammatic representation for visualizing and measuring advancing and receding contact angles θ_a and θ_r when implementing a dip coating technique in step c) of the manufacturing method of the invention, illustrating three configurations a to c;

Figures 8a, 8b and 8c diagrammatically show three different regimes appearing when the withdrawing speed U from a dip coating bath continuously increases from figure 8a to figure 8c, only figure 8a with U lower than a critical speed U_c being according to the invention;

Figure 9 is a diagrammatic representation showing an exemplary embodiment for implementing steps a) and b) of the method of the invention applied to a hydrophobic first abrasion-resistant coating via a mask-assisted etching technique to obtain the surface wettability pattern comprising the two-dimensional array;

Figure 10 is a diagrammatic representation showing an exemplary embodiment for implementing step c) of the method of the invention by dip coating and withdrawing the two-dimensional array obtained in figure 9 in and from a hydrophilic liquid;

Figure 11 is a photograph of a mask usable in the mask-assisted etching technique of step b), made of a flexible plastic film provided with a pattern of micro-holes, which mask is laminated on a flat lens;

Figure 12 is a photograph of another mask usable in the mask-assisted etching technique of step b), made of a flexible plastic film provided with a pattern of micro-holes, which mask is laminated onto a curved surface of an ophthalmic lens blank; and

Figure 13 is a photograph of a curved ophthalmic lens incorporating a three-dimensional array of micro-lenses obtained by a mask and method according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0066] In the present description, the terms "comprise" (and any grammatical variation thereof, such as "comprises" and "comprising"), "have" (and any grammatical variation thereof, such as "has" and "having"), "contain" (and any grammatical variation thereof, such as "contains" and "containing"), and "include" (and any grammatical variation thereof, such as "includes" and "including") are open-ended linking verbs. They are used to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps or components or groups thereof. As a result, a method, or a step in a method, that "comprises," "has," "contains," or "includes" one or more steps or elements possesses those one or more steps or elements, but is not limited to possessing only those one or more steps or elements.

[0067] Unless otherwise indicated, all numbers or expressions referring to quantities of ingredients, ranges, reaction conditions, etc. used herein are to be understood as modified in all instances by the term "about." Also unless otherwise indicated, the indication of an interval of values « from X to Y » or "between X to Y", according to the present invention, means as including the values of X and Y.

Total and partial wetting of hydrophilic and hydrophobic areas/ zones of a surface

[0068] As shown in figures 1 and 2, a hydrophilic liquid covering a totally (figure 1) or partially (figure 2) wettable area can be described thermodynamically by the wetting parameter S , with $S = \gamma_{SG} - \gamma_{LG} - \gamma_{LS}$, where γ_{SG} , γ_{LS} and γ_{LG} represent the solid-vapor, solid-liquid and liquid-vapor interfacial energies, respectively.

[0069] When $S > 0$ in the total wetting case of figure 1, the liquid completely spreads on the surface with a macroscopic contact angle equal to zero, whereas when $S < 0$ in the partial wetting case of figure 2, the liquid only partially spreads on the surface and forms a droplet with a macroscopic contact angle θ less than 90° . The macroscopic contact angle θ is a common measure of the surface ability to be partially wetted or totally wetted by a liquid, and the wetting parameter S only depends upon the interfacial surface energy of the system.

[0070] When the contact angle is lower than 90° , preferably lower than 80° , more preferably lower than 70° , the surface is said to be hydrophilic, being almost totally wettable when the contact angle is lower than e.g. 20° , as is the case for each hydrophilic micro-area patterned in step b) and coated in step c) according to the method of the invention.

[0071] But when the contact angle is greater than 90° , the surface is said to be non-wettable (i.e. hydrophobic), although physically it is a partial wetting (super repellent or non-wettable surfaces typically have a contact angle higher than 120°), as is the case shown in figure 3 for the at least one hydrophobic zone connecting the hydrophilic micro-areas to each other.

[0072] Figure 4 shows an exemplary surface wettability pattern obtained in step b) according to the invention, this pattern comprising mutually distant hydrophilic micro-areas 1 which are each configured to form a droplet D after step c), and at least one hydrophobic zone 2 which connects the hydrophilic micro-areas 1 to each other, so as to form a

two-dimensional array 3 and the resulting pattern. When increasing the volume of each droplet D, the contact line is blocked by the hydrophilic frontier between the micro-areas 1 and the zone 2 until it reaches a limit contact angle θ_c where the droplet D starts to spread beyond the frontier.

[0073] This limit contact angle θ_c gives the maximum curvature radius of each micro-lens, considering a base diameter and assuming a perfectly spherical shape for each droplet D.

[0074] If the droplet base diameter is below twice the capillary radius l_c , then the shape of each droplet D is not affected by gravity:

$$l_c = \sqrt{\frac{\gamma}{(\rho g)}}$$

[0075] The capillary radius is generally about 1 mm, and the droplet diameter according to the invention is below 2 mm when the droplets are spherical, since their shape is dominated by capillary forces. A droplet diameter of more than 2 mm may be slightly flattened by gravity, and is therefore not preferred in the present invention.

Dynamic formation of droplets by the dip coating technique

[0076] The formation of droplets on the surface wettability pattern 3 obtained in step b), which comprises the hydrophilic micro-areas 1 and the at least one hydrophobic zone 2 on the first abrasion-resistant coating, occurs during withdrawal of this pattern 3 from the bath of hydrophilic liquid, after which the at least one hydrophobic zone 2 remains dry and the droplets D are finally anchored to the hydrophilic micro-areas 1.

[0077] On the partially wettable zone (hydrophobic zone 2, hence $S < 0$), the maximum speed of withdrawal is related to the transition speed U. When the viscous dragging forces are higher than the capillary force, the contact line is no more stable, and the metastable created film may lead to an uncontrolled dewetting from the hydrophobic zone. This situation, which is not controllable and cannot provide a satisfactory control of the uniformity of the droplets volume, is avoided in the present invention as explained below.

[0078] To implement step c) in the method of the invention, advancing and receding contact angles (which are distinct and define a contact angle hysteresis by the difference between them) during dip coating are taken into account and measured, as explained in figure 7. Specifically, dip coating involves a receding contact angle, which receding contact angle is measured with a common apparatus (for instance by a needle as visible in both intermediate drawings of figure 7, or by a tilting technique as visible in bottom drawing c of figure 7).

[0079] This contact angle should be high enough to leave the hydrophobic zone totally not wetted after a slow withdrawal of the patterned surface 3 from the bath of hydrophilic liquid. Indeed, for a partially wetting liquid, two regimes exist depending upon complex fluid mechanic physics:

- if the surface 3 is totally dry, then no liquid film is drained onto the surface; or
- the surface 3 drains the liquid, which then undesirably either forms a continuous film or breaks into small droplets.

[0080] According to the invention, in order to successfully form the array of micro-lenses in steps c) and d), the partially wettable portion (i.e. the hydrophobic zone 2) must be left dry after dip coating, and the inventors have established to this occurred only below a determined transition speed that cannot be easily predicted but was easily measured.

[0081] Qualitatively, the inventors checked that the higher the contact angle was on the partially wettable portion or hydrophobic zone 2, the higher the withdrawal transition speed was allowed. For productivity, high contact angles (greater than 70°, preferably greater than 80°, more preferably greater than 90°, even better greater than or equal to either of the following values 95° and 100°) are preferred, but are not absolutely required for the hydrophobic zone 2.

[0082] Because a liquid film was only formed locally on the surface of the wettable areas, the withdrawal speed determined the amount of liquid left on these totally wetted parts (hydrophilic micro-areas 1).

[0083] Turning to figure 4, assuming the contact angle was zero on the wettable hydrophilic micro-areas 1, the maximum droplet size was restricted by the advancing and receding contact angles on the partially wettable parts (hydrophobic zone 2) of the patterned surface 3.

[0084] The higher the contact angle was between liquid and solid on the partially wettable hydrophobic zone 2, the lower the minimum droplet radius was.

[0085] The maximum droplet contact angle θ_c was the advancing contact angle onto partial wetting area of the lens surface. If the implemented angle θ was significantly greater than θ_c , then the droplets D spread on the partial wetting zone 2, which was not desired for the method of the invention.

[0086] As visible in figure 8, too high a withdrawal speed resulted in leaving too much liquid on the surface 3, which

did not satisfy the above-described criterion for droplet stability. As the critical transition speed can be expressed with the critical capillary number C_a^* by means of the withdrawal speed:

$$C_a = \frac{\eta U}{\gamma}$$

it follows that the critical transition speed may as expressed below:

$$U^* = \frac{\gamma C_a^*}{\eta}$$

[0087] This number compares the viscous dragging force to the surface tension.

[0088] Under the critical transition speed U , the partially wettable hydrophobic zone 2 remained dry, no liquid being dragged onto the zone 2 and the contact line was stable, as illustrated in the left drawing of figure 8, which was the only one to represent a well-controlled withdrawal according to the invention.

[0089] But above the critical transition speed U , the contact line significantly rose and as a consequence a layer of liquid was undesirably dragged on the surface, as illustrated in the right drawing of figure 8.

[0090] Finally, droplets D of the hydrophilic liquid were successfully anchored onto the sole hydrophilic micro-areas 1 corresponding to the highest solid/liquid interfacial energy with the wetting parameter $S > 0$ (total wetting), and the higher the withdrawal speed, the higher the volume and the lower the curvature radius for each droplet D.

Microstructured surface(s) of an ophthalmic article according to the invention

[0091] In the present description, the microstructured surface(s) which form(s) the front main surface and/or the rear main surface of the ophthalmic substrate 10 provided with the first abrasion-resistant coating include lenslets in the form of micro-lenses, which form bumps separated by recesses at the main surface they are arranged onto. The outline of the lenslets may be round or polygonal, for example circular, elliptic or hexagonal, even though any outline may be contemplated for the droplets D, and the micro-lenses may be spherical, toric, or have an aspherical shape, rotationally symmetrical (i.e. axisymmetric or not), although any shape may also be contemplated for the micro-lenses. Each micro-lens may have a single focus point, or cylindrical power, or non-focusing point.

[0092] In the exemplary embodiment of figure 5 which illustrates a case of non-circular boundary for the droplet D and due to capillary forces, the droplet surface adopts a shape that minimizes its air/surface area, i.e. in this example an elliptic outline which defines an hemi-ellipsoidal shape having two different orthogonal radii or curvatures (close to a torical surface if the radii are small enough). This hemi-ellipsoidal shape created two focal points. These outline and shape may be numerically calculated, and this boundary condition may be precisely controlled by the method of the invention.

[0093] In preferred embodiments, lenslets or micro-lenses can be used to prevent progression of myopia or hyperopia. In that case, the base lens substrate comprises a base lens providing an optical power for correcting myopia or hyperopia, and the micro-lenses or the lenslets may provide respectively an optical power greater than the optical power of the base lens if the wearer has myopia, or an optical power lower than the optical power of the base lens if the wearer has hyperopia.

[0094] Lenslets may have a contour shape being inscribable in a circle having a diameter greater than or equal to 500 μm and preferably of between 1 mm and 2 mm in case the micro-lenses are designed for controlling evolution of myopia.

[0095] Lenslets may have a height, measured in a direction perpendicular to the main surface they are arranged onto, that is greater than or equal to 0.1 μm and less than or equal to 50 μm .

[0096] The main surface can be defined as a surface, that can be a plano, spherical, sphero-cylindrical or even complex surface, that includes the central point of every microstructures. This main surface can be a virtual surface, when microstructures are embedded in the lens or close or identical to the ophthalmic lens physical outer surfaces when microstructures are not embedded. The height of the microstructure can be then determined using local perpendicular axis to this main surface, and calculating for the each point of the microstructure the difference between the maximum positive deviation minus the minimum negative deviation to the main surface, along the axis.

[0097] Lenslets may have periodical or pseudo periodical layout, but may also have randomized positions. Exemplary layouts for lenslets may be a grid with constant grid step, honeycomb layout, multiple concentric rings, contiguous e.g. no space in between microstructures.

[0098] These structures may provide optical wave front modification in intensity, curvature, or light deviation, where

the intensity of wave front is configured such that structures may be absorptive and may locally absorb wave front intensity with a range from 0% to 100%, where the curvature is configured such that the structure may locally modify wave front curvature with a range of +/- 20Diopters, and light deviation is configured such that the structure may locally scatter light with angle ranging from +/- 1° to +/- 30°.

[0099] A distance between structures may range from 0 (contiguous) to 3 times the structure (separate microstructures).

[0100] As visible in Figure 6, the method of the invention for manufacturing an ophthalmic article for controlling the evolution of myopia, by means of the three-dimensional array of micro-lenses, used micro-lenses with a diameter d of about 1-2 mm and an optical power of 3 diopters.

[0101] The sag (also called "sagitta") of the micro-lenses could be calculated from the well-known equation:

$SAG = R - \sqrt{R^2 - (d/2)^2}$, where R denotes the radius of Curvature and d the diameter.

[0102] The sag was at most a few μm , and the droplet contact angle was very small : since $\tan \theta \sim \theta$ for small angles, θ was close to few mrad (1mrad $\sim 0.06^\circ$). This angle was very small, and this factor was found to be non-limiting in practice.

EXAMPLES FOR IMPLEMENTATION OF METHODS OF THE INVENTION:

[0103] The following examples illustrate the present invention in a more detailed, but non-limiting manner.

Process implemented for the dip coating of surface wettability patterns

[0104] As explained above, the surface wettability pattern was immersed into a preferentially low viscosity and high surface tension hydrophilic liquid to limit viscous drag and maximize capillary forces, which restrained the liquid from wetting the partially wettable surface defined by the hydrophobic zone 2 (which repelled the hydrophilic liquid).

[0105] Since the volume of each droplet to be obtained was very small, the coating material was indeed diluted to allow good control of the droplets D and resulting micro-lens final volume, after solvent evaporation. The solvent was selected to lower the viscosity of the hydrophilic liquid and to increase its surface tension, thus promoting a very low drag force. In the tested solvent-based hydrophilic coating, the subsequent drying slightly changed the volume of the droplets D which were more flattened (thus inducing a change of curvature radius), which change was easily anticipated.

[0106] After a slow withdrawal of the surface wettability pattern from the hydrophilic bath, the withdrawal speed was slightly increased, and the transition withdrawal speed - where no liquid (film or droplet) was drained from the partially wettable surface - was measured. This was done on the not-patterned surface, but preferably the transition withdrawal speed should be measured also on the real surface wettability pattern.

[0107] This value of the transition speed was the limiting maximum withdrawal speed of the dip coating process, i.e. a critical transition speed where the liquid started to be anchored onto the sole totally wettable hydrophilic micro-areas 1. The withdrawal speed and dry content of the liquid was thus adjusted, to obtain the desired droplets and micro-lenses height after solvent evaporation and drying/curing. The actual withdrawal speed never exceeded the critical speed thus measured.

[0108] The three-dimensional array of micro-lenses obtained in step d) was allowed to dry and could subsequently be cured if needed, for instance by UV radiation or heat.

Exemplary implementation of steps a), b), c) and d) on this basis

[0109] A stencil-type masking film of vinyl having a $90\mu\text{m}$ thickness was cut with a pattern of holes representing a 2D view of the array of micro-lenses to be finally obtained (see the photograph of figure 11). The holes had a diameter of between 1 mm and 2 mm in view of the ophthalmic design to be manufactured. Then, the following main steps were implemented.

[0110] The masking film was then cold pressed onto a main surface of a curved ophthalmic lenses (see figure 12) consisting of an CR 39[®] lens substrate provided with a first abrasion-resistant coating defining this main surface which was hydrophobic. The first abrasion-resistant coating used in first and second experiments was as disclosed in example 3 of document FR 2 702 486 A1 (or its equivalent US 2003/165698 A1), and exhibited a Bayer value, measured in accordance with the ASTM F735-81 standard, which was of between 2 and 4.

[0111] The low module of the masking film facilitated this pressing operation, even though slight heating with hot air could be used to avoid wrinkles.

[0112] A second film was applied onto the other main surface of the ophthalmic substrate opposite the first abrasion-resistant coating, in order to protect the substrate from the subsequent chemical treatment.

[0113] The entire lens thus protected was then immersed in a bath of light etching caustic chemicals of NaOH (KOH was alternatively used in another experiment), for a slight chemical etching of the surface of the first abrasion-resistant coating. The lens was then washed and the second film was removed. The purpose of caustic etching was to remove the fluorinated surfactant present on the surface on the first abrasion-resistant coating, and also to create the surface

wettability pattern to be achieved in step b) of the method of the invention, with the two-dimensional array of hydrophilic micro-areas 1 obtained by this caustic etching through the holes of the masking film and the hydrophobic zone 2 (untreated by caustic etching) which connects the micro-areas 1 to each other.

[0114] The lens was then immersed in a bath of hydrophilic liquid designed to form the second abrasion-resistant coating, which was almost identical to the formulation of the first abrasion-resistant coating, except that the hydrophilic liquid did not contain any surfactant (whereas the first abrasion-resistant coating comprised a fluorinated surfactant to enhance its wettability on the substrate).

[0115] As explained above, the hydrophilic liquid was withdrawn below a critical withdrawal speed from the liquid bath, so that this liquid did not wet the hydrophobic zone 2 and was anchored to the sole hydrophilic micro-areas 1. Afterwards, the three-dimensional array of micro-lenses appeared spontaneously, and was subsequently allowed to dry and harden. The Bayer value of the second abrasion-resistant coating, measured in accordance with the ASTM F735-81 standard, was of between 2 and 4.

[0116] Figure 13 shows a photograph of an ophthalmic lens incorporating the three-dimensional array of micro-lenses thus obtained by the method of the invention.

Claims

1. Method for manufacturing an ophthalmic article having a front main surface and a rear main surface, at least one of which is a microstructured surface, the method comprising the following steps:
 - a) Providing an ophthalmic substrate (10) with a substrate surface which is either hydrophobic or hydrophilic;
 - b) Patterning the substrate surface to create thereon a surface wettability pattern comprising a two-dimensional array (3) of mutually distant hydrophilic micro-areas (1) and of at least one hydrophobic zone (2) which separates the hydrophilic micro-areas (1) from each other;
 - c) Coating the two-dimensional array (3) with a hydrophilic liquid which is able to form an abrasion-resistant coating in a dried and/or cured state, to form mutually distant droplets (D) of the hydrophilic liquid which are anchored to the hydrophilic micro-areas (1) by wettability thereof; and
 - d) Drying and/or curing the mutually distant droplets (D) of the hydrophilic liquid, to generate therefrom a three-dimensional array of micro-lenses forming the at least one microstructured surface.
2. Method according to claim 1, wherein step a) comprises rendering the ophthalmic substrate (10), which consists of a mineral material, either hydrophobic or hydrophilic on said substrate surface.
3. Method according to claim 1, wherein step a) comprises providing the ophthalmic substrate (10), which consists of an organic material, with a first abrasion-resistant coating which is either hydrophobic or hydrophilic and defines said substrate surface, and wherein preferably in step c) the hydrophilic liquid is selected so that the abrasion-resistant coating forming the micro-lenses, or second abrasion-resistant coating, has a Bayer value greater than or equal to the Bayer value of the first abrasion-resistant coating, both Bayer values being measured in accordance with the ASTM F735-81 standard and being preferably greater than or equal to 2.
4. Method according to any of preceding claims, wherein in step c) the hydrophilic liquid is a polar liquid selected from solutions in a polar solvent and emulsions comprising a polar phase.
5. Method according to claim 4, wherein in step c) the hydrophilic liquid comprises at least one inorganic oxide of a metal or non-metal selected from colloidal silica, titania, zirconia, antimony oxide and mixtures thereof, and wherein the hydrophilic liquid is selected from polar solutions comprising alcoholic, ketones and/or ester solvents, the hydrophilic liquid comprising an epoxysilane hydrolyzate, the at least one inorganic oxide and a catalytic amount of an aluminum-based curing catalyst.
6. Method according to any of preceding claims, wherein step c) is implemented by dip coating, by dipping the ophthalmic substrate (10) provided with the substrate surface once patterned into a bath of the hydrophilic liquid and afterwards by a controlled withdrawal of the dipped ophthalmic substrate (10) from the bath, the withdrawal being controlled so as to obtain a desired curvature radius and/or volume for each of the micro-lenses obtained in step d).
7. Method according to claim 6, wherein in the dip coating of step c), a maximum allowable withdrawal speed is determined, by measuring a critical transition speed where no film of the hydrophilic liquid is dragged onto the at least one hydrophobic zone (2) once dipped and withdrawn,

and wherein the controlled withdrawal of the dipped ophthalmic substrate (10) from the bath is implemented at an adjusted withdrawal speed selected to be lower than or equal to said critical transition speed.

8. Method according to claim 6 or 7, wherein steps b) and c) are implemented so that the micro-lenses obtained in step d) have at least one greater transverse direction, such as a diameter, which is greater than 500 μm and preferably of between 1 mm and 2 mm in case the micro-lenses are designed for controlling evolution of myopia when the ophthalmic article is an ophthalmic curved prescription lens.

9. Method according to any of preceding claims, wherein

- the ophthalmic substrate (10) consists of a mineral material, or of an organic material which is thermosetting, photocurable or thermoplastic; and wherein
- the method further comprises at least one of steps A) and B):

A) coating the ophthalmic substrate (10) before step a) with a primer coating which is itself provided with said substrate surface, and

B) laminating the ophthalmic substrate provided with the patterned substrate surface on an existing curved lens, by a forming technique implemented by laminating

- between step b) and step c), the ophthalmic substrate (10) provided with said substrate surface patterned according to the surface wettability pattern (3), or

- after step d), the ophthalmic substrate (10) provided with the patterned substrate surface and the three-dimensional array of micro-lenses.

10. Method according to any of preceding claims, wherein the method further comprises the following steps:

e) removing the three-dimensional array of micro-lenses obtained in step d) by dipping in a removing bath and optionally providing said substrate surface with protective masking means, so as to selectively recover the ophthalmic substrate (10) provided with the substrate surface, and

f) implementing the sequence of steps b), c) and d) at least once, to obtain another three-dimensional array of micro-lenses forming the at least one microstructured surface.

11. Method according to any of preceding claims, wherein step a) is implemented by using, by way of the ophthalmic substrate (10) provided with said substrate surface, an ophthalmic lens selected from a finished ophthalmic lens and an ophthalmic lens blank optionally edged, preferably an ophthalmic curved prescription lens.

12. Method according to any of preceding claims, wherein step b) is implemented by a mask-assisted or maskless technique selected from chemical etching, laser ablation or etching, low pressure or atmospheric plasma or corona etching, UV or ozone etching, Reactive Ion Etching (RIE) and chemical grafting of molecules bearing hydrophilic or hydrophobic functions, to create the hydrophilic micro-areas (1) and the at least one hydrophobic zone (2) on said substrate surface.

13. Method according to claim 12, wherein step b) is implemented by a mask-assisted technique by

(i) patterning said substrate surface which is selected to be hydrophobic, preferably by a chemical etching technique assisted with a flexible mask (20) applied under pressure onto the substrate surface, or by

(ii) beforehand providing in step a) the substrate surface with an outer surface which is either already hydrophilic or is rendered hydrophilic between steps a) and b), and creating in step b) the at least one hydrophobic zone (2) via said mask-assisted technique by treating unmasked areas with said molecules bearing hydrophobic functions.

14. Method according to claim 13, wherein step a) comprises providing the ophthalmic substrate (10), which consists of an organic material, with a first abrasion-resistant coating which is hydrophobic and defines said substrate surface, wherein step b) is implemented in case (i) by providing the flexible mask (20) with an array of through micro-holes optionally having different shapes and/or dimensions, the through micro-holes preferably having a diameter of between 1 mm and 2 mm, and by immersing the first abrasion-resistant coating in a caustic bath of NaOH or KOH, and wherein in case (ii), the outer surface of the first abrasion-resistant coating is rendered hydrophilic between steps a) and b) by:

- at least one of chemical etching, laser ablation or etching, low pressure or atmospheric plasma or corona etching, UV or ozone etching and Reactive Ion Etching (RIE), and chemical grafting of molecules bearing hydrophilic functions, or by
- depositing onto the first abrasion-resistant coating a hydrophilic layer comprising at least one inorganic oxide of a metal or non-metal selected from silica, titania, zirconia, antimony oxide and mixtures thereof.

15. Ophthalmic article obtained by a method according to any of claims 1-14, wherein the ophthalmic article has a front main surface and a rear main surface, at least one of which is a microstructured surface, and comprises:

- an ophthalmic substrate (10) provided with a patterned substrate surface which is patterned according to a surface wettability pattern (3) comprising mutually distant hydrophilic micro-areas (1) and of at least one hydrophobic zone (2) which separates the hydrophilic micro-areas (1) from each other, and
- a three-dimensional array of micro-lenses which form the at least one microstructured surface and are respectively anchored to the sole hydrophilic micro-areas (1), the micro-lenses being based on an abrasion-resistant coating which coats the patterned substrate surface, and
- in case the ophthalmic substrate (10) consists of an organic material, said substrate surface is defined by a first abrasion-resistant coating which is patterned according to said surface wettability pattern (3), said abrasion-resistant coating being a second abrasion-resistant coating which coats the patterned first abrasion-resistant coating and which preferably has a Bayer value greater than or equal to the Bayer value of the first abrasion-resistant coating, both Bayer values being measured in accordance with the ASTM F735-81 standard.

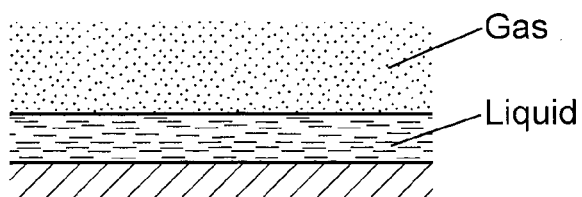


FIG. 1

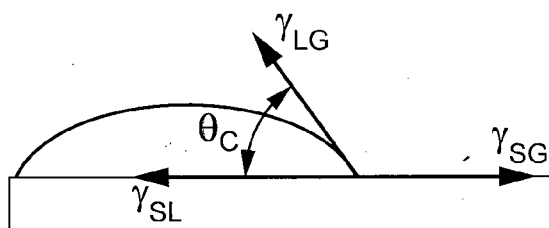


FIG. 2

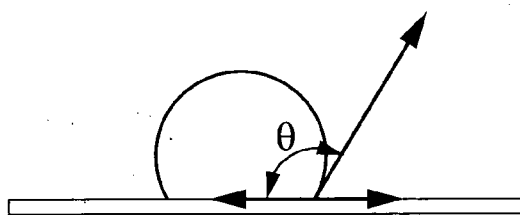


FIG. 3

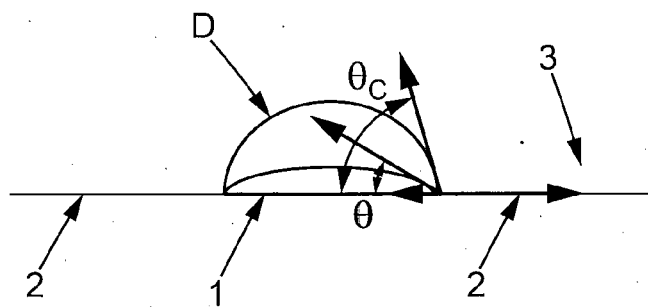


FIG. 4

FIG. 5

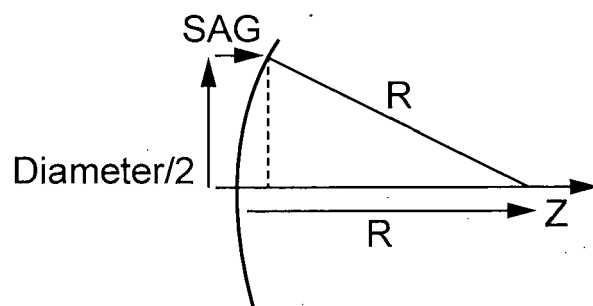
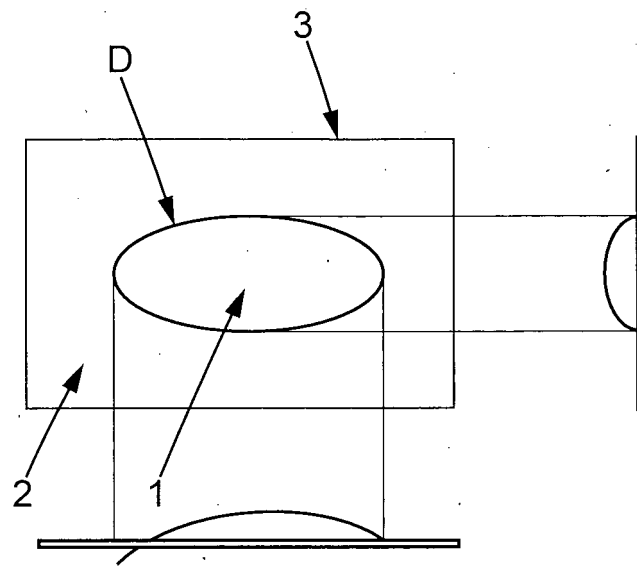


FIG. 6

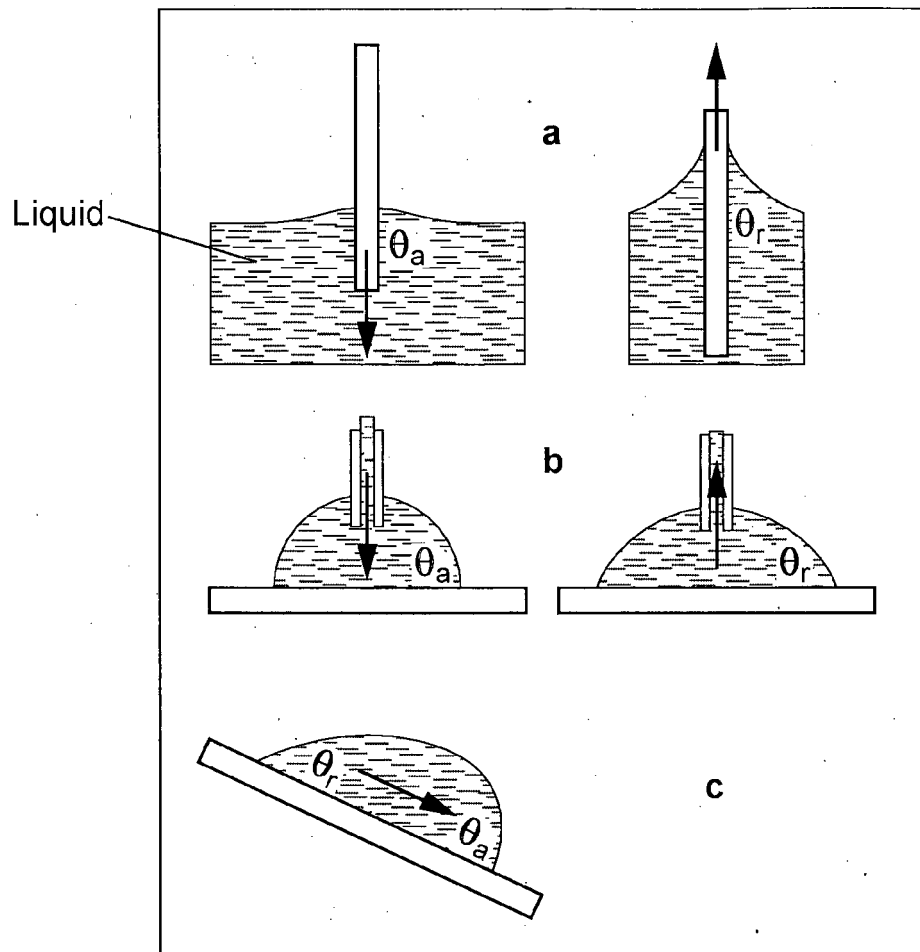


FIG. 7

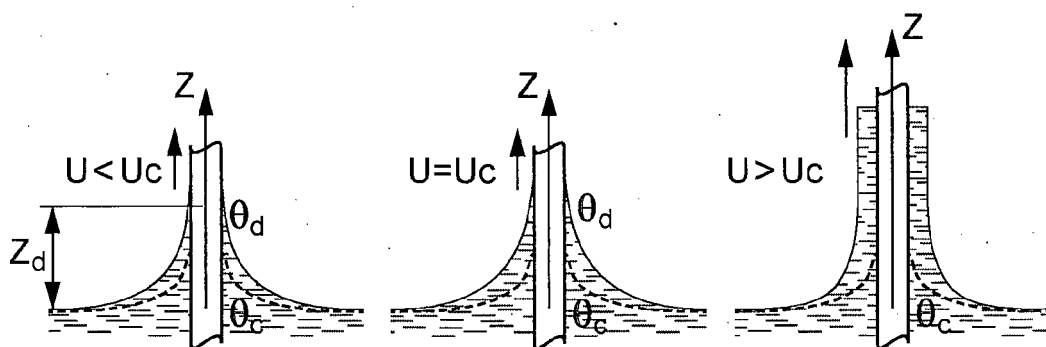


FIG. 8

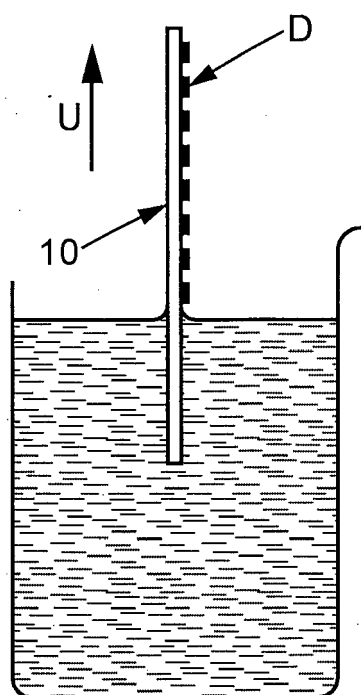
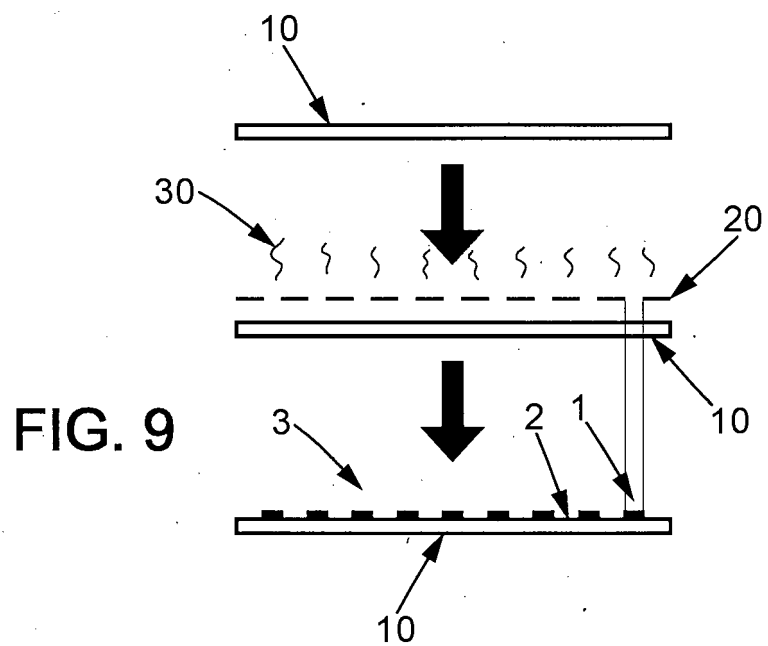


FIG. 10

FIG. 11

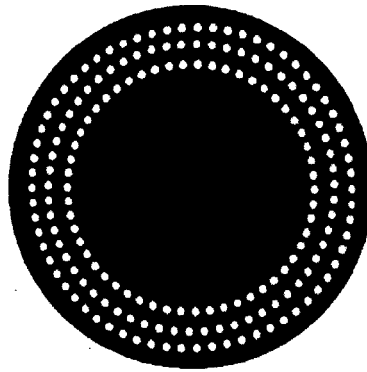


FIG. 12

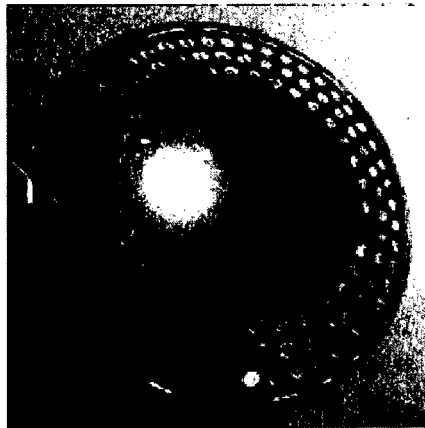
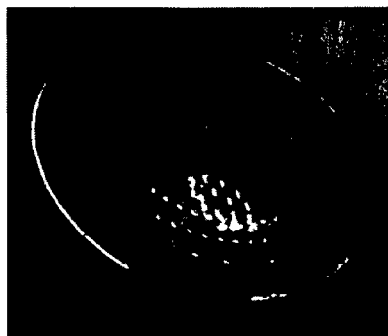


FIG. 13





EUROPEAN SEARCH REPORT

Application Number

EP 22 31 5268

5

10

15

20

25

30

35

40

45

50

55

3

EPO FORM 1503 03:82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
E	EP 4 091 805 A1 (ESSILOR INT [FR]) 23 November 2022 (2022-11-23) * paragraphs [0002], [0003], [0005], [0006], [0099], [0129] - [0138], [0142], [0144], [0150], [0162]; figures *	1-5, 15	INV. B29D11/00
A	WO 2021/209527 A1 (ESSILOR INT [FR]) 21 October 2021 (2021-10-21) * paragraph [0143]; figures *	1-15	
A	EP 3 640 714 A1 (ESSILOR INT [FR]) 22 April 2020 (2020-04-22) * paragraphs [0002] - [0008] *	1-15	
A	WO 00/66353 A1 (UNIV NORTH CAROLINA STATE [US]; SAKHRANI VINAY [US] ET AL.) 9 November 2000 (2000-11-09) * page 11, line 11 - page 12, line 13 *	1-15	
A	WO 2008/114893 A1 (UNIV NAT CHONNAM IND FOUND [KR]; PARK SI-HYUN [KR]; SON SU-GWANG [KR]) 25 September 2008 (2008-09-25) * page 8, lines 16-21 *	1-15	TECHNICAL FIELDS SEARCHED (IPC) B29D
A	US 9 709 819 B2 (ESSILOR INT [FR]) 18 July 2017 (2017-07-18) * column 1, lines 18-52 * * column 11, lines 21-40 *	1-15	
A	WO 2021/255007 A1 (NILT SWITZERLAND GMBH [CH]) 23 December 2021 (2021-12-23) * paragraphs [0063] - [0096]; figures *	1-15	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 12 May 2023	Examiner Klinger, Thierry
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 22 31 5268

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-05-2023

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 4091805 A1	23-11-2022	EP 4091805 A1	23-11-2022
		WO 2022243207 A2	24-11-2022
WO 2021209527 A1	21-10-2021	AU 2021255892 A1	27-10-2022
		BR 112022020238 A2	22-11-2022
		CA 3179031 A1	21-10-2021
		CN 115380228 A	22-11-2022
		EP 4136484 A1	22-02-2023
		KR 20230004481 A	06-01-2023
		WO 2021209527 A1	21-10-2021
EP 3640714 A1	22-04-2020	BR 112021007076 A2	20-07-2021
		CN 112912789 A	04-06-2021
		EP 3640714 A1	22-04-2020
		US 2021354410 A1	18-11-2021
		US 2023072785 A1	09-03-2023
		WO 2020078691 A1	23-04-2020
WO 0066353 A1	09-11-2000	AU 4467400 A	17-11-2000
		US 6582823 B1	24-06-2003
		WO 0066353 A1	09-11-2000
WO 2008114893 A1	25-09-2008	KR 20080085402 A	24-09-2008
		WO 2008114893 A1	25-09-2008
US 9709819 B2	18-07-2017	CN 104718083 A	17-06-2015
		EP 2903831 A1	12-08-2015
		FR 2996163 A1	04-04-2014
		US 2015277143 A1	01-10-2015
		WO 2014053716 A1	10-04-2014
WO 2021255007 A1	23-12-2021	EP 4165470 A1	19-04-2023
		WO 2021255007 A1	23-12-2021

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2020078964 A1 [0007] [0029]
- FR 2702486 A1 [0029] [0110]
- US 2003165698 A1 [0029] [0110]

Non-patent literature cited in the description

- **DANIEL M. HARTMANN ; OSMAN KIBAR ; SADIK C. ESENER.** Characterization of a polymer microlens fabricated by use of the hydrophobic effect. *OPTICS LETTERS*, 01 July 2000, vol. 25 (13), 975 [0008]